

# PATENT SPECIFICATION

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NO DRAWINGS

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## (54) IMPROVEMENTS IN ANTI-CORROSIVE PAINTS

(71) We, HENKEL & CIE, GMBH, a German Company, of 67, Henkelstrasse, 4000 Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to anti-corrosive paints.

The application of the so-called metal dust colours to metals, preferably iron, as paints for protection against corrosion from the effects of the weather and water, using alkali metal silicates as binders, is known. Zinc dust paints are specially suitable for this purpose. However, metal dust from aluminium, lead or copper is also suitable as pigment, the latter being used usually in admixture with zinc dust. Such points are extremely effective and resistant as corrosion protection agents. Their preparation and use in practice, however, is subject to the difficulty that the mixtures of alkali metal silicate solutions and metal dust, especially zinc dust, needs to be used within a relatively short time, since the components react relatively quickly with the evolution of hydrogen. Therefore difficulties exist in keeping such agents in closed containers, and also in their transportation.

Inhibitors which delay the reaction between the alkali metal silicate solution and the zinc dust are known, but the results are often not satisfactory for practical requirements. For example, if lead oxide and sodium persulphate are added to such paints, the evolution of hydrogen does not occur until after about 24 hours. This is frequently still insufficient for practical requirements, however.

More recently, a process has become known with the keeping quality of such mixtures (so-called "pot life") can be considerably improved. This improvement can be brought about by an addition of alkali metal chromate and organic compounds which contain at least 2 amino groups in the molecule.

The present invention provides a metal-dust-containing anti-corrosive paint compris-

ing an organic nitro compound which is soluble in an aqueous alkali metal silicate solution, boric acid or a salt thereof, and an alkali metal silicate as binder.

Suitable organic nitro compounds are aliphatic nitro compounds such as nitromethane or nitro-acetic acid and aromatic nitro compounds such as nitrobenzoic acid, nitrophenols or dinitrophenols, nitroresorcinol or nitro pyrocatechol. Compounds such as nitro-urea and nitro-guanidine can also be used. The position of the substituents in the aromatic ring of the aromatic organic nitro compounds is not critical. Preferred organic nitro-compounds are nitromethane, nitrobenzoic acid and nitrophenol, and the nitro compounds can be used either individually or in admixture.

The organic nitro components are used in quantities of 0.1 to 5, preferably 0.4 to 1.2% by weight, referred to solid alkali metal silicate.

The paints according to the invention also have a content of boric acid or a salt thereof, for example potassium, sodium, or ammonium borate. These compounds are added in quantities of 0.5 to 3, preferably 0.8 to 1.5% by weight, referred in each case to solid alkali metal silicate.

The organic nitro compounds and the boric acid or a salt thereof may be added in the form of solutions or in some cases in solid form, to the metal dust paints during or after the preparation. The metal dust paints are prepared in known way by mixing alkali metal silicate solution with metal dust, especially zinc dust. Sodium or potassium silicate solutions such as commercial waterglass solutions with a molar ratio of  $\text{Na}_2\text{O} : \text{SiO}_2$  of from 1: 3.2 to 3.8 and a concentration of about 28 to 42°Bé may be used.

When alkali metal silicate solutions with a molar ratio of alkali metal oxide:  $\text{SiO}_2$  of from 1:3.8 to 1:4.4 are used, metal dust agents particularly resistant to corrosion are obtained. Such alkali metal silicate solutions can be very easily spread and are easy to handle when they contain an addition of about 0.1—2% by weight of certain quaternary

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ammonium compounds. Water-soluble quaternary ammonium bases are suitable which contain an alkyl residue having 1 to 4 carbon atoms and three further alkyl or alkanol residues having 1 to 12 carbon atoms. Tetraethylammonium hydroxide is preferably used as the additive.

Furthermore, the metal dust paints, especially zinc dust paints, may also contain thickeners such as alginates, methylcellulose and starch in quantities which amount from 0.01 to 0.3% by weight, based on the total mixture. In some cases it is also advantageous to add emulsifiers in small quantities, preferably up to about 0.5% by weight. Especially prepared emulsifiers are addition products of ethylene oxide to fatty alcohols or fatty acids.

Fillers such as kaolin, bentonite and montmorillonite and zinc oxide may also be added to the paints.

The metal dust paints, especially zinc dust paints, of the above-described type, which contain additives according to the invention, have a "pot life" of more than three weeks, i.e. no measurable evolution of hydrogen takes place before this period, when they are stored in non-metallic containers. It is also possible to use in these paints very fine zinc dust, which usually reacts even with distilled or tap water. The use of zinc dust of this kind is desirable when specially water-resistant paints are to be obtained. The water-resistance can also be further improved by use of alkali metal metal silicate solutions with a high proportion of  $\text{SiO}_2$ .

#### EXAMPLE 1

300 g of alkali metal silicate solution (molar ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  1: 3.8;  $\text{SiO}_2$  content 22.4% by weight) are mixed with a dispersion of 45 g of water, 0.9 g of boric acid and 0.3 g of 2, 6-dinitrophenol to give a clear solution.

1.1 kg of zinc dust (zinc content 99.2%; particle size 2—4  $\mu$ ) are stirred with 240 g of the binder so obtained at room temperature. The zinc dust paint obtained can be used immediately by spreading or spraying on. After storing for three weeks in a plastic container it can still be used in the same way without loss of quality after it is stirred up.

If instead of boric acid and dinitrophenol, 0.3 g of hexamethylene tetramine and 1.2 g of potassium chromate are used as an additive to the alkali metal silicate solution, the zinc dust paint can only be kept for about two weeks.

#### EXAMPLE 2.

If with a method of operation as in Example 1, 1 g of sodium borate and 0.3 g of nitromethane or 0.5 g of *p*-nitrophenol are used as addition to the alkali metal silicate

solution, a zinc dust paint is also obtained which is stable in the container for at least three weeks.

#### EXAMPLE 3.

3 g of a 20% tetraethylammonium hydroxide solution are dissolved with 1 g of ammonium dichromate, mixed in 24 g of ion-free water and the mixture is stirred into 215 g of waterglass (molar ratio of  $\text{SiO}_2:\text{Na}_2\text{O}$  3.8: 1, solids content 29%).

0.6 g of boric acid and 0.2 g of *o*-nitrobenzoic acid are further added and the binder so produced is stirred with 1100 g of zinc dust (zinc content 99.2%; particle size 2—4  $\mu$ ). A zinc dust paint stable in the container over several weeks is obtained which has good spreadability and only a short setting time.

#### EXAMPLE 4.

Paints made up as in Example 3, except that the *o*-nitrobenzoic acid was replaced by an equivalent amount of dinitrophenol, nitroresorcinol, nitropyrocatechol, nitrourea or nitroguanidine also gave satisfactory results.

#### WHAT WE CLAIM IS:—

1. A metal-dust-containing anti-corrosive paint comprising an organic nitro group-containing compound which is soluble in aqueous alkali metal silicate solution, boric acid or a salt thereof, and an alkali metal silicate as binder.

2. A paint as claimed in claim 1 in which the organic nitro group-containing compound is present in an amount of from 0.1 to 5% by weight based on the solid alkali metal silicate.

3. A paint as claimed in Claim 2 in which the organic nitro group-containing compound is present in an amount of from 0.4 to 1.2% by weight based on the solid alkali metal silicate.

4. A paint as claimed in any of claims 1 to 3 in which boric acid or a salt thereof is present in an amount of from 0.5 to 3% by weight based on the solid alkali metal silicate.

5. A paint as claimed in Claim 4 in which the boric acid or a salt thereof is present in an amount of from 0.8 to 1.5% by weight based on the solid alkali metal silicate.

6. A paint as claimed in any of Claims 1 to 5 in which the organic nitro group-containing compound is nitrobenzoic acid and/or nitrophenol, and/or nitromethane.

7. A paint as claimed in Claim 6 having a content of from 0.5 to 3% by weight of boric acid and from 0.1 to 5% by weight of nitrobenzoic acid and/or nitrophenol and/or nitromethane, based on the solid alkali metal silicate.

8. A paint as claimed in any of Claims 1 to 7 in which the molar ratio of alkali metal oxide:  $\text{SiO}_2$  is from 1:3.8 to 1:4.4.

9. A paint as claimed in any of claims 1 to 8 which further has from 0.1 to 2% by weight, based on the solid alkali metal silicate, of a quaternary ammonium base having one alkyl residue of from 1 to 4 carbon atoms and three further alkyl or alkanol residues of from 1 to 12 carbon atoms.
10. A paint as claimed in claim 9 in which the quaternary ammonium salt is tetraethylammonium hydroxide.
11. A paint as claimed in any of claims 1 to 10 which further has a content of from 0.01 to 0.3% by weight based on the total mixture of a thickener.
12. A paint as claimed in any of claims 1 to 11, which further has up to 0.5% by weight of an emulsifier.
13. A paint as claimed in claim 12 where- in the emulsifier is an addition product of ethylene oxide to fatty alcohols or fatty acids.
14. A paint as claimed in claim 1, sub- stantially as hereinbefore described with refer- ence to Example 1, 2 or 3.
15. A paint as claimed in claim 1, sub- stantially as hereinbefore described with refer- ence to Example 4.

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